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Quantifying osmotic membrane fouling to enable comparisons across diverse processes

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In this study, a method of in situ membrane fouling quantification is developed that enables comparisons of foulant accumulation between desalination processes with different membranes, driving forces, and feed solutions. Unlike the conventional metric of flux decline, which measures the response of a process to fouling, the proposed method quantifies the foulant accumulation. Foulant accumulation is parameterized by two variables, cake structural parameter and hydraulic diameter, that are calculated from flux measurements using a model for salt and water transport through fouled reverse osmosis (RO) and forward osmosis (FO) membranes, including dispersive mass transfer in the FO membrane support layer. Model results show that pressure declines through the foulant layer and can, in FO, reach negative absolute values at the membrane. Experimental alginate gel fouling rates are measured within a range of feed ionic compositions where cake hydraulic resistance is negligible. Using both flux decline and cake structural parameter as metrics, the effect of feed salinity on RO fouling is tested and RO is compared to FO. When RO is fouled with alginate, feed salinity and membrane permeability affect flux decline but not foulant accumulation rate. Between FO and RO, the initial rates of foulant accumulation are similar; however, FO exhibits slower flux decline, which causes greater foulant accumulation over time. The new methodology enables meaningful quantification and comparison of fouling rates with the aim of improving fundamental understanding of fouling processes.

1. Introduction

Although osmotic separation processes such as reverse osmosis (RO) are the most energy-efficient water treatment technologies for a wide range of water compositions [1–3], they are plagued by membrane fouling. A recent review by She et al. [4] discussed a range of fouling types, flux decline models, and mitigation methods. To understand the factors that govern membrane fouling and develop mitigation strategies, many studies have compared different processes, coatings, etc. using flux decline as a metric. Flux decline (the change in flux due to fouling divided by the initial flux) quantifies the effect of fouling on the productivity of a given process, but does not give any insight into the accumulation of foulant itself. Therefore, when studies compare different processes such as RO and forward osmosis (FO) using flux decline alone, differences in the response of the processes to foulant accumulation preclude meaningful comparisons. In order to translate experimental results into fundamental understanding of membrane fouling, a deposit-centric, in situ fouling quantification method is needed.

In this paper, a method is outlined for quantifying porous foulant accumulation on semipermeable membranes in terms of two parameters that capture both osmotic and hydraulic causes of flux decline. FO and RO models are developed, although other osmotic processes (assisted forward osmosis, etc.) could be treated similarly if the active layer is facing the feed. The type of fouling considered is porous fouling, which could consist of biofouling, organic fouling, or inorganic fouling so long as no crystals pierce the membrane's active layer and the active area is not blocked by oil deposition or crystal growth. Here, alginate is used as a model porous foulant because of its gelation in the presence of calcium ions and the strong dependence of its material properties on its ionic environment. The proposed method is used to quantify fouling in experimental RO and FO.

1.1. Limitations of flux decline

Many fouling studies are concerned with comparisons, such as the relative fouling propensity of FO vs. RO [5], pressurized vs. unpressurized FO [6,7], or new membrane coatings vs. commercial membranes [8]. Although flux decline comparisons often keep initial flux constant because of the dependence of fouling rate on flux [9], differences in membrane properties and solution composition can lead

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to differences in flux decline between experiments even if the foulant layers are identical in size and structure. Flux decline effectively measures the response of the system to fouling; however, it can only hint at the quantity of accumulated foulant.

As an example, Lee et al. [5] compare fouling with colloidal silica and various dissolved organics in FO and RO, and find that FO has more severe flux decline in most cases. However, they claim that the faster flux decline in FO is primarily due to the increase in osmotic pressure near the membrane that is enhanced by reverse salt diffusion from the draw solution to the feed solution. Because of the reverse salt diffusion in FO, no conclusion could be drawn about the relative accumulation rates of foulants in FO and RO by observing flux decline alone. Rather than continue to make comparisons in terms of flux decline and speculate on how those results relate to fouling propensity, this paper provides a framework using flux measurements to quantify the amount of foulant accumulated as a function of time.

1.2. Existing methods of quantifying fouling

Some methods have been developed based on the hydraulic resistance to flow through the porous foulant cake. Hydraulic resistance is generally the main cause of flux decline for membranes with large pores (e.g., ultrafiltration), which do not reject small dissolved species, but this assumption is sometimes extended to salt-rejecting membranes such as RO. For example, Farias et al. [10] quantify fouling with a "membrane fouling index" based on a (hydraulic) resistance in series model presented by Nguyen et al. [11] for ultrafiltration membranes. However, methods such as this neglect to account for another important factor in flux decline of semipermeable membranes: the concentration of dissolved constituents within the cake layer and the resulting increase in osmotic pressure at the membrane.

For salt-rejecting membranes such as FO and RO, this concentrative mechanism of flux decline has been described by Hoek and Elimelech [12]: When a porous cake layer forms on a salt-rejecting membrane, diffusion of salt away from the membrane must counter the flux of salts toward the membrane due to convection with the feed. In this way, the cake layer causes an increase in the osmotic pressure at the membrane active layer, reducing the driving force for water flux according to the solution–diffusion model [13]. As with more porous membranes, there is also some hydraulic resistance to permeation of water through the foulant cake layer, which is accounted for in the Hoek and Elimelech model [12]. This model quantifies foulant accumulation in terms of the osmotic pressure differential across the cake, which they term "cake enhanced osmotic pressure" (CEOP). The CEOP model is useful when making comparisons at a fixed salinity within a fixed process (e.g., seawater RO). However, changes in salinity will affect the osmotic pressure differential for a given foulant cake, so it cannot be used to compare fouling at different salinities (between wastewater RO and seawater RO, for example).

The path toward a universal model has been laid out by these existing studies, which we build on using a layered transport model that accounts for both hydraulic and concentrative causes of flux decline in FO and RO. We take an approach similar to Nagy's model for flux in unfouled FO membranes [14], but incorporate the presence of a porous foulant layer with gradients in both hydraulic and osmotic pressure. We reduce the problem of quantification to two parameters: cake structural parameter (analogous to the support layer structural parameter in FO membranes) and pore hydraulic diameter. Using this model, fouling tests spanning a range of membranes, processes, and feed compositions can be compared directly to improve fundamental understanding of fouling processes. We then experimentally compare accumulation rates of alginate gel fouling across two dimensions that take advantage of the comparison capabilities of the new quantification method: (1) the effect of feed salinity in RO and (2) the difference between FO and RO with the same feed solution.

2. Layered transport model for fouled RO and FO

Modeling the effects of fouling in osmotic separation processes is challenging due to widely ranging length scales, complex geometries, and spatially varying material properties. As a simplification, we model quasi-steady, one-dimensional transport of salt and water perpendicular to the membrane in both FO and RO. Real membranes and foulant layers may have indistinct and/or rough interfaces, but this model divides the flow path into distinct, planar layers, each with its own transport model. In many ways, the model developed here parallels the model of Nagy [14] for FO without fouling. Like Nagy, we model transport of a single salt in one dimension through several layers with their own appropriate models, but we add a layer of porous foulant on the feed-facing side of the membrane and also account for dispersion in the FO membrane support layer.

Fig. 1 depicts the layers considered and their respective transport models. Feed and draw/permeate concentrations in the bulk flow are treated as boundary conditions. Because salt and water

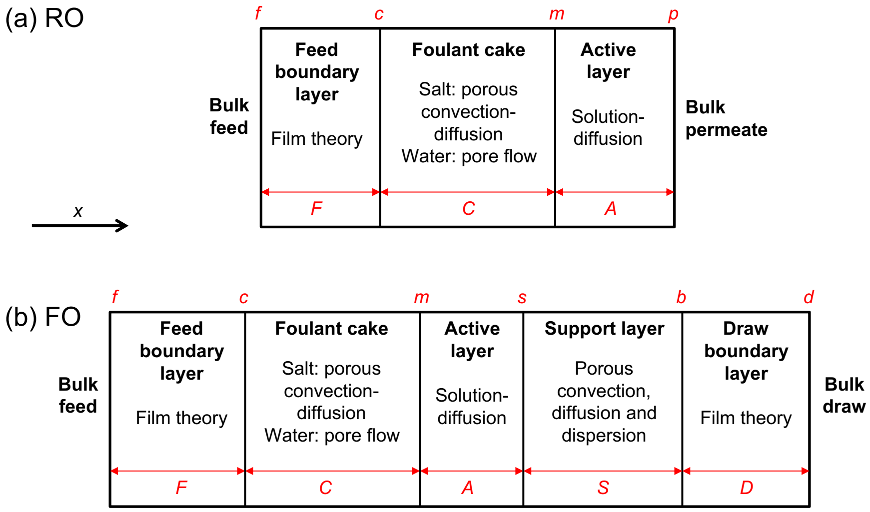

Fig. 1. Summary of layers and their respective models for (a) RO and (b) FO, with water flow from left to right. Boundary conditions (bulk feed, draw and permeate), the positive x direction for all modeling, and subscripts (in red) used to denote layers and interfaces are labeled. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)